### Gas Separation Hot Paper

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## A Metal–Organic Framework with Suitable Pore Size and Specific Functional Sites for the Removal of Trace Propyne from Propylene

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**Abstract:** Separation of propyne/propylene  $(C_3H_4/C_3H_6)$  is more difficult and challenging than that of acetylene/ethylene  $(C_2H_2/C_2H_4)$  because of their closer molecular sizes. A comprehensive screening of a series of metal-organic frameworks with broad types of structures, pore sizes, and functionalities was carried out. UTSA-200 was identified as the best separating material for the removal of trace  $C_3H_4$  from  $C_3H_4$  $C_{3}H_{6}$  mixtures. Gas sorption isotherms reveal that UTSA-200 exhibits by far the highest  $C_3H_4$  adsorption capacity (95 cm<sup>3</sup> cm<sup>-3</sup> at 0.01 bar and 298 K) and record  $C_3H_4/C_3H_6$ selectivity, which was mainly attributed to the suitable dynamic pore size to efficiently block the larger  $C_3H_6$  molecule whilst the strong binding sites and pore flexibility capture smaller  $C_{3}H_{4}$ . This material thus provides record purification capacity for the removal of  $C_3H_4$  from a 1:99 (or 0.1:99.9, v/v)  $C_3H_4$  $C_3H_6$  mixture to produce 99.9999 % pure  $C_3H_6$  with a productivity of 62.0 (or 142.8)  $mmolg^{-1}$ .

Adsorptive separation based on porous materials opens the door to enable a possible transition from traditional energyintensive cryogenic distillation to the energy-efficient adsorbent-based separation for industrial gas separation and purification.<sup>[1]</sup> Compared to conventional activated carbons and zeolites, the emerging microporous metal–organic frame-

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works (MOFs) have attracted immense attention for gas separation/purification in recent years owing to their fascinating tunability with respect to pore size, shape, and surface functionality.<sup>[2]</sup> These features have enabled us to design target materials with the on-demand pore size and functionality for diverse gas separation and purification, including separation of  $CO_2/N_2$ ,  $CO_2/CH_4$ , light hydrocarbons,  $C_2H_2/CO_2$ ,  $O_2/N_2$ ,  $CO/CO_2$ , and so on.<sup>[3]</sup>

Gas molecules with quite different molecular weights and thus vapor pressures or boiling points, for example, CO<sub>2</sub> and N<sub>2</sub>, can be easily separated because of their different interactions with porous materials.<sup>[4]</sup> Those gas molecules with similar molecular weights and vapor pressures are difficult and challenging to be separated.<sup>[5]</sup> Ultramicroporous MOFs are superior to well-developed porous materials for gas separation/purification; this superiority is attributed to their power of the finely tuned pores to enforce the sieving effects and the readily immobilized functional sites on the pore surfaces to introduce the specific recognition with one of the gas molecules, and the interplay of dual functionalities of both the suitable size and functional site.<sup>[6,7]</sup> Indeed, a few ultramicroporous MOFs have been discovered for the very challenging separations of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> over the past several years.<sup>[7]</sup> Compared with the separation of  $C_2H_2/C_2H_4$ , the  $C_3H_4/C_3H_6$  separation is more difficult and challenging. As shown in Scheme 1, acetylene and ethylene are the simplest alkyne and alkene with a three-dimensional (3D) size of  $3.32 \times 3.34 \times 5.70$  and  $3.28 \times 4.18 \times 4.84$  Å<sup>3</sup>, respectively. The kinetic diameter difference between  $C_2H_2$  (3.3 Å) and  $C_2H_4$  (4.2 Å) is about 0.9 Å.<sup>[8]</sup> Propyne and propylene, also known as methylacetylene and



**Scheme 1.** Comparison of molecular size and kinetic diameter difference of  $C_2H_2/C_2H_4$  and  $C_3H_4/C_3H_6$ .

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methylethylene, have a larger size of  $4.16 \times 4.01 \times 6.51$  and  $4.65 \times 4.16 \times 6.44$  Å<sup>3</sup>. C<sub>3</sub>H<sub>4</sub> is a linear molecule, and C<sub>3</sub>H<sub>6</sub> has a curved shape. Despite different shapes, the relatively bulky methyl group makes the kinetic diameter difference between the pair C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> (4.2 and 4.6 Å) much closer (nearly 0.4 Å) than C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>.<sup>[2a]</sup> The smaller the size difference between the pair of molecules is, the more difficult the separation will be.

Removal of trace  $C_3H_4$  (1000 or 10000 ppm) from  $C_3H_4$ / C<sub>3</sub>H<sub>6</sub> mixtures is one of the most important separation processes to produce polymer-grade C<sub>3</sub>H<sub>6</sub> gas (the C<sub>3</sub>H<sub>4</sub> impurity should be lower than 5 ppm), a prime olefin raw material for petrochemical production. Microporous materials for C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> separation have not been well-explored, with only the ELM-12, SIFSIX-3-Ni (SIFSIX = hexafluorosilicate  $(SiF_6^{2-})$  and ZU-62 having been reported.<sup>[9]</sup> While these materials exhibit high C<sub>3</sub>H<sub>4</sub> adsorption capacity, they only exhibit moderately high gas-separation performance because of the comparatively large pores to include both  $C_3H_4$ and C<sub>3</sub>H<sub>6</sub> molecules, thus limiting the productivity of the desired C3H6 product. Targeting high performance porous materials can not only significantly enhance the C3H6 productivity, but also increase the purity of the C<sub>3</sub>H<sub>6</sub> product, thus reduce the energy cost for this important industrial separation. Adsorption selectivity and uptake capacity are the two most important criteria that are directly related to productivity and purity, but it is very difficult to target materials with both high values (so-called trade-off). To realize high selectivity and adsorption uptake simultaneously, ideal MOFs should have suitable pore size and specific functionality that can discriminate the difference in size and physical properties between the two molecules. While rational design of microporous MOFs with desired high productivity for  $C_3H_4/C_3H_6$  separation is quite difficult, we thus systematically screened a series of porous MOFs with different structures, pore sizes, and pore-surface functionalities for this separation. To our surprise, the material UTSA-200 ([Cu(azpy)<sub>2</sub>(SiF<sub>6</sub>)]<sub>n</sub>, azpy = 4,4'-azopyridine),<sup>[7b]</sup> which we recently realized for the highly efficient  $C_2H_2/C_2H_4$  separation, turned out to be very powerful as well for the more difficult  $C_3H_4/C_3H_6$  separation. Our detailed studies comprehensively affirm its benchmark separation performance with the record  $C_3H_4$  uptake capacity (95 cm<sup>-3</sup> cm<sup>-3</sup> at 0.01 bar and 298 K), gas selectivity (over 20000), and  $C_3H_6$  productivity (62.0 and 142.8 mmol g<sup>-1</sup> for 1:99 and 0.1:99.9 mixtures).

We first selected 20 different MOFs to examine their C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> adsorption properties and then superficially evaluate their separation potential (see the Supporting Information, Table S1 for detailed structural parameters). As shown in the Supporting Information, Figure S1, achieving the looked-for efficient separation is indeed very challenging for  $C_3H_4/C_3H_6$  separation, and the examined MOFs almost show unsatisfactory separation properties. Despite the daunting challenge, some reported MOFs with strong binding sites toward C3H4 (SIFSIX-1-Cu, SIFSIX-2-Cu-i, SIFSIX-3-Ni, and ELM-12) exhibit steep adsorption of C<sub>3</sub>H<sub>4</sub> at the lowpressure region over C<sub>3</sub>H<sub>6</sub>, leading to the benchmark selectivity reported so far. However, their pore sizes allow the passage of both  $C_3H_4$  and  $C_3H_6$ , thus delimiting their high gas selectivities.<sup>[9]</sup> UTSA-200, with a smaller aperture size of 3.4 Å, exhibits an exceptionally high C<sub>3</sub>H<sub>4</sub> uptake but very little  $C_3H_6$  adsorption at the low-pressure region (Figure 1), offering the potential to be the best candidate for  $C_3H_4/C_3H_6$ separation.



Figure 1. a) The pore aperture and pore chemistry of SIFSIX materials. b) Associated  $C_3H_4$  and  $C_3H_6$  adsorption isotherms at 298 K.

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Structural analysis revealed that pore sizes in SIFSIX-1-Cu, SIFSIX-2-Cu-i, and SIFSIX-3-Ni range from microporous (8.0 Å) to ultra-microporous (4.2 Å, Figure 1a),<sup>[7a, 10]</sup> indeed allowing both C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> to enter the pores. The doubly interpenetrated UTSA-200 possesses much smaller channels of 3.4 Å.<sup>[7b]</sup> This static pore size is notably less than both of  $C_3H_4$  and  $C_3H_6$ , which might induce the selective sieving toward the larger C3H6 molecules when the framework flexibility and thus slightly enlarged pore sizes are taken into the account. Furthermore, there exist a large number of  $SiF_6^{2-}$  anions around the channels that show much stronger binding affinity toward alkynes over alkenes.<sup>[7a,9b]</sup> These structural features on UTSA-200 might be responsible for the exceptional performance for  $C_3H_4/C_3H_6$  separation. Bulk purity of UTSA-200 sample was confirmed by powder X-ray diffraction (PXRD) patterns and the measured surface area (Supporting Information, Figure S2).<sup>[11]</sup>

All of these SIFSIX materials show steep and high  $C_3H_4$  uptakes over  $C_3H_6$  at 298 K (Figure 1 b). When the pore size was gradually reduced from SIFSIX-1-Cu to UTSA-200, the  $C_3H_4$  sorption isotherms at low-pressure region (0–0.01 bar) become steeper and steeper (Figure 2 a). The  $C_3H_4$  capture capacity at 0.01 bar increases in the order of SIFSIX-1-Cu < SIFSIX-2-Cu-I < SIFSIX-3-Ni < UTSA-200 (Figure 2 b), wherein UTSA-200 shows the highest value of 95 cm<sup>3</sup>cm<sup>-3</sup>. Even under an ultralow  $C_3H_4$  partial pressure (1000 ppm), the  $C_3H_4$  uptake capacity of UTSA-200 can reach 83 cm<sup>3</sup> cm<sup>-3</sup>, still notably higher than SIFSIX-3-Ni (75 cm<sup>3</sup> cm<sup>-3</sup>). SIFSIX-2-Cu-i (11 cm<sup>3</sup> cm<sup>-3</sup>), and ZU-62 (5.2 cm<sup>3</sup> cm<sup>-3</sup>). In comparison to other top-performing materials, UTSA-200 also sets

new benchmarks at both 0.01 and 0.001 bar (Figure 2c; Supporting Information, Figure S3), making it the most promising material for the trace  $C_3H_4$  removal. In contrast, UTSA-200 shows an ignorable  $C_3H_6$  uptake at 0.01 bar (Figure 2b), and little  $C_3H_6$  uptake up to 0.4 bar (10.5 cm<sup>3</sup> cm<sup>-3</sup>), which is dramatically lower than SIFSIX-2-Cu-i (61.2 cm<sup>3</sup> cm<sup>-3</sup>), SIFSIX-3-Ni (85.1 cm<sup>3</sup> cm<sup>-3</sup>) and ZU-62 (69.7 cm<sup>3</sup> cm<sup>-3</sup>) at 0.4 bar. The fine-tuned pore size of UTSA-200 indeed supports the molecular exclusion of  $C_3H_6$  at low pressures. Most importantly, the sieving effect of  $C_3H_6$  can be strengthened with the temperature increased to 318 K while the low-pressure  $C_3H_4$  uptake capacity can be retained (Supporting Information, Figure S5), indicating its bright promise for  $C_3H_4/C_3H_6$  separation at a broader operation temperature.

Ideal adsorbed solution theory (IAST) was utilized to calculate the adsorption selectivity of these materials for a 1:99 (v/v)  $C_3H_4/C_3H_6$  mixture at 298 K. UTSA-200 exhibits an extraordinary high selectivity of over 20000 (Figure 2 d; Supporting Information, Figure S7), significantly higher than the previous benchmark ELM-12 (83), SIFSIX-3-Ni (76), and ZU-62 (48). It should be noted that the selectivity of UTSA-200 can be only used for the qualitative comparison. As shown in the Supporting Information, Figure S8, the uptake ratio of  $C_3H_4/C_3H_6$  for UTSA-200 at 0.01:0.01 and 0.01:0.99 bar can reach 149.5 and 2.49, respectively. Both values are the highest among the indicated MOFs, further confirming its best  $C_3H_4/C_3H_6$  selectivity. Furthermore, UTSA-200 also exhibits the record  $C_3H_4$  uptake (2.88 mmolg<sup>-1</sup>) for adsorption from this mixture (Figure 2e).



*Figure 2.* a) Experimental  $C_3H_4$  and  $C_3H_6$  adsorption isotherms of SIFSIX-2-Cu-i (black), SIFSIX-3-Ni (blue), and UTSA-200 (red) at 298 K in the region of 0–0.05 bar. b) Comparison of  $C_3H_4$  and  $C_3H_6$  uptake at 0.01 bar for the SIFSIX materials. c) A comparison of  $C_3H_4/C_3H_6$  uptake ratio at 0.01:0.01 bar for UTSA-200 and other indicated MOFs. d) IAST selectivity and e) IAST calculated  $C_3H_4$  uptake capacity of the indicated MOFs from 1:99 (v/v) gas mixtures. f) DFT-D calculated structure and binding site of UTSA-200 $\subset_3H_4$ . The different nets are highlighted in purple and gray for clarity. Cu cyan, Si dark green, F red, N blue, C gray, H white, C in  $C_3H_4$  orange.

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To understand the origin of the ultra strong C<sub>3</sub>H<sub>4</sub> adsorption and effective C<sub>3</sub>H<sub>6</sub> sieving, we performed detailed modeling studies using first-principles dispersion-corrected density functional theory (DFT-D) method on UTSA-200. The static pore size of UTSA-200, based on the crystal structure, is about 3.4 Å,<sup>[7b]</sup> which is much smaller than both  $C_3H_4$  (4.2 Å) and  $C_3H_6$  (4.6 Å).<sup>[2a]</sup> As shown in the Supporting Information, Figure S9, after adsorption of C<sub>3</sub>H<sub>4</sub> molecules, the N=N bond and pyridine rings on the azpy exhibit an obvious rotation and distortion, which enlarges the pore to about 4.2 Å, thereby allowing the passing of a  $C_3H_4$  molecule. Calculations also show that each adsorbed C3H4 molecule is bound by two SiF<sub>6</sub><sup>2-</sup> sites from different nets through cooperative C-H…F and C=H…F H-bonding, with the short distance of 2.179 and 2.239/2.459 Å (Figure 2 f). Owing to the larger size of C<sub>3</sub>H<sub>6</sub>, the pore needs to be expanded more for the passage (Supporting Information, Figure S10). The calculated static binding energies for C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> are 62.3 kJ mol<sup>-1</sup> and 45.4 kJ mol<sup>-1</sup>, respectively. The framework thus has much stronger binding with C3H4 molecule than C<sub>3</sub>H<sub>6</sub>, as further confirmed by the higher experimental isosteric heat of adsorption  $(Q_{st})$  for  $C_3H_4$  (Supporting Information, Figure S11). This kind of subtle guest-assisted pore opening is primarily dictated by the interaction strength of the adsorbate framework: the stronger the intermolecular interactions are, the lower the gate-opening pressure will be.<sup>[6b,12]</sup> Therefore, attributed to the smaller size and the stronger interactions with the framework, C<sub>3</sub>H<sub>4</sub> molecule might open the pore easily to result in the ultrastrong  $C_3H_4$ adsorption. Conversely, the larger size and weaker interactions of  $C_3H_6$  molecule make the pore opening more difficult and thereby to be size-excluded, especially at the lowpressure region.

High-resolution neutron powder diffraction (NPD) measurements were further performed on a  $C_3D_4$ -loaded sample of UTSA-200 at 298 K to confirm the calculated  $C_3H_4$  binding sites. The data indicate that  $C_3D_4$  adsorption indeed induced a lot of local framework distortion in the sample (to accommodate the large gas molecules), resulting in lower overall crystal symmetry. Consequently, it became impractical to perform a rigorous Rietveld refinement of the NPD data. Fortunately, it is still possible to qualitatively compare the experimental data with the simulated NPD pattern based on a model structure built upon the DFT-D calculation results. As shown in the Supporting Information, Figure S12, the two agree reasonably well, and thus strongly support the validity of the DFT-D determined  $C_3H_4$  binding configuration.

Transient breakthrough simulations were first conducted for UTSA-200 and the indicated MOFs in fixed-bed adsorption processes to determine the feasibility of  $C_3H_4/C_3H_6$ separation. The 1:99 (v/v)  $C_3H_4/C_3H_6$  mixture was employed as feeds to mimic the industrial process conditions. As depicted in Figure 3 a, efficient separations were realized with all the examined MOFs, whereby  $C_3H_6$  first eluted through the bed to yield a polymer-grade gas, and then  $C_3H_4$ broke through from the bed at a certain time  $\tau_{break}$ . Owing to the record selectivity and  $C_3H_4$  uptake capacity, UTSA-200 exhibits the longest  $\tau_{break}$  value, several times higher than that in SIFSIX-3-Ni, ELM-12, and ZU-62 (Supporting Information, Figure S13). During the time  $0-\tau_{break}$ , the pure  $C_3H_6$ 



*Figure 3.* a) Transient breakthrough simulations of  $C_3H_4/C_3H_6$  (1:99, v/v) mixture on UTSA-200 versus some benchmark materials at 298 K. b) Plots of the productivity of pure  $C_3H_6$  from  $C_3H_4/C_3H_6$  mixtures in the simulated breakthrough for the indicated MOFs. c) Experimental breakthrough curves for 1:99 (v/v) mixture under a flow of 2.0 mLmin<sup>-1</sup> at 298 K and 1.01 bar. d) The  $C_3H_6$  productivity from  $C_3H_4/C_3H_6$  mixtures of the indicated MOFs, with  $C_3H_4$  concentration less than 1 ppm. e) Experimental breakthrough curves for a 0.1:99.9 (v/v) mixture. f) Retained time of  $C_3H_6$  in cycling tests of UTSA-200 for a 1:99 (v/v) mixture.

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productivity by UTSA-200 can reach  $367.2 \text{ mol } \text{L}^{-1}$  (Figure 3b), which is notably higher than that of SIFSIX-3-Ni, ZU-62, and ELM-12.

Experimental breakthrough studies were performed in a packed column of activated UTSA-200 under flow  $(2.0 \text{ mLmin}^{-1})$  of binary C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> (1:99, v/v) mixtures at 298 K, and compared with the indicated MOFs. The breakthrough data depicted in Figure 3c clearly demonstrate that UTSA-200 can effectively separate  $C_3H_4/C_3H_6$  mixtures: the C<sub>3</sub>H<sub>6</sub> gas passed through the adsorption bed immediately, while C3H4 was retained in the packed column over 710 min  $g^{-1}$ . This breakthrough time of  $C_3H_4$  is three times longer than that of SIFSIX-2-Cu-i, ELM-12, and SIFSIX-3-Ni. These experimental data are consistent well with the simulated results. The concentration of C3H4 in the outlet effluent was even below 1 ppm up to 700 min (Supporting Information, Figure S14), which is notably less than the acceptable level of less than 5 ppm for polymer-grade  $C_3H_6$ gas. It is to be noted that this deep removal of  $C_3H_4$  from 1:99 (v/v) mixture is unable to be achieved for most selected MOFs (such as MOF-74 series, Cu-BTC, ZIF-8, MIL-100) owing to their unsatisfied selectivity (Supporting Information, Figure S15). Among the viable MOFs, the C<sub>3</sub>H<sub>6</sub> production of UTSA-200 from the outlet effluent for a given cycle was calculated to be record high of  $62.9 \text{ mmol g}^{-1}$  (Figure 3d; Supporting Information, Table S14), far exceeding those observed in SIFSIX-3-Ni (19.6 mmolg<sup>-1</sup>) and ELM-12  $(15.8 \text{ mmol g}^{-1})$ . For C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> mixture containing ultralow  $C_3H_4$  concentration (1000 ppm), UTSA-200 also exhibits the best separation performance with the record C<sub>3</sub>H<sub>6</sub> production of 143.8 mmol g<sup>-1</sup>, as illustrated in Figure 3e and the Supporting Information, Table S15. Finally, the separation performance of UTSA-200 can be recycled at least 7 times (Figure 3 f; Supporting Information, Figures S17–S22).

Through a comprehensive screening of broad types of MOFs, we demonstrated herein an ultra-microporous MOF, UTSA-200, as the best separating material for the removal of trace  $C_3H_4$  from  $C_3H_4/C_3H_6$  mixtures. The foregoing results revealed that UTSA-200 exhibits both the unprecedented high C<sub>3</sub>H<sub>4</sub> capture capacity and separation selectivity, setting new benchmarks for any material reported so far. This exceptional separation performance is attributed to the framework flexibility originated from the rotation of pyridine rings inside the pores and the strong binding sites that can selectively block the larger C<sub>3</sub>H<sub>6</sub> but capture large amount of the preferred smaller C<sub>3</sub>H<sub>4</sub> at low-pressure region. Breakthrough experiments confirmed that UTSA-200 can completely remove trace  $C_3H_4$  from 1:99 and 0.1:99.9 (v/v) mixtures, affording the record-high C<sub>3</sub>H<sub>6</sub> production scale with 99.9999% purity. This work not only reports the best porous material for C3H4/C3H6 separation, but also demonstrates that framework flexibility can be utilized to target some very challenging gas separations, thus fully fulfilling the promise of emerging microporous MOFs for gas separations in the future.

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### Conflict of interest

The authors declare no conflict of interest.

Keywords: gas separation  $\cdot$  porous materials  $\cdot$  propylene purification  $\cdot$  propyne  $\cdot$  size sieving

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